



## Evaluation of the Effectiveness of Hydrophobic Microbeads for Diethyl Phthalate Removal from Aqueous Solution

### Hidrofobik Mikrokürelerin Sulu Çözeltilerden Dietilfitalat Uzaklaştırma Etkinliğinin Değerlendirilmesi

Bilgen Osman<sup>✉</sup> and Elif Tümay Özer<sup>\*</sup>

Department of Chemistry, Faculty of Arts and Science, Bursa Uludağ University, Bursa, Turkey.

#### ABSTRACT

In this study, hydrophobic poly(divinylbenzene-N-methacryloyl-L-tryptophan methyl ester) [poly(DVB-MATrp)] microbeads (average diameter = 150-200  $\mu\text{m}$ ) were used for diethyl phthalate (DEP) removal from aqueous solution. The poly(DVB-MATrp) microbeads were synthesized by suspension polymerization. The microbeads were used for DEP adsorption from aqueous solution to determine the effect of pH, initial DEP concentration, temperature and contact time on the adsorbed amounts of DEP. The effect of initial DEP concentration was investigated in the concentration range of 1-300 mg/L at pH 3.0. The experiments were conducted at three different temperatures (25°C, 35°C and 45°C). The maximum DEP adsorption capacity was calculated as 251.3 mg/g at pH 3.0 (25°C). The adsorbed amount of DEP onto the poly(DVB-MATrp) was decreased with increasing temperature due to the exothermic nature of the adsorption. The kinetic studies demonstrated that the adsorption process reached equilibrium at around 30 min. The Langmuir isotherm model fitted the adsorption data. The pseudo-first-order and pseudo-second-order kinetic models were employed to evaluate the adsorption process. The prepared microbeads were repeatedly used for DEP adsorption without a significant change in the adsorption capacity. The poly(DVB-MATrp) microbeads were also effectively used in bottled, and tap water samples spiked with DEP.

#### Keywords

Diethyl phthalate, adsorption, microbead, endocrine disruptor.

#### ÖZ

Bu çalışmada, hidrofobik poli(divinilbenzen-N-metakriloil-L-triptofan metil ester) [poli(DVB-MATrp)] mikroküreler (ortalama çap: 150-200  $\mu\text{m}$ ) sulu fazdan dietil fitalat (DEP) uzaklaştırılması için kullanıldı. Poli(DVB-MATrp) mikroküreler süspanسیون polimerizasyonu ile sentezlendi. Mikroküreler pH, başlangıç DEP derişimi, sıcaklık ve temas süresinin adsorplanan DEP miktarına etkisinin belirlenmesi amacıyla sulu çözeltilerden DEP adsorpsiyonunda kullanıldı. Başlangıç DEP derişiminin etkisi 1-300 mg/L (pH 3.0) derişim aralığında araştırıldı. Deneşler üç farklı sıcaklıkta (25°C, 35°C and 45°C) gerçekleştirildi. Maksimum DEP adsorpsiyon kapasitesi pH değeri 3.0 olan sulu çözeltilerde 251,3 mg/g (25°C) olarak hesaplandı. Adsorpsiyonun ekzotermik doğasından dolayı poli(DVB-MATrp) mikroküreler üzerine adsorplanan DEP miktarı artan sıcaklıkla azalış gösterdi. Kinetik çalışmaları adsorpsiyonun yaklaşık 30 dakikada dengeye ulaştığını kanıtladı. Adsorpsiyon Langmuir izoterm modeline uygun olarak gerçekleşti. Adsorpsiyon verilerinin değerlendirilmesi için yalancı-birinci derece ve yalancı-ikinci derece kinetik modeller kullanıldı. Hazırlanan mikroküreler DEP adsorpsiyon kapasitesinde belirgin bir değışiklik olmaksızın tekrar tekrar kullanıldı. Poli(DVB-MATrp) mikroküreler aynı zamanda DEP katılmış şişe suyu ve çeşme suyu örneklerinde etkin olarak kullanıldı.

#### Anahtar Kelimeler

Dietilfitalat, adsorpsiyon, mikroküre, endokrin bozucu.

**Article History:** Received: Aug 16, 2018; Revised: Jan 29, 2019; Accepted: Jan 30, 2019; Available Online: Mar 01, 2019.

**DOI:** 10.15671/HJBC.2019.277

**Correspondence to:** E.T. Özer, Department of Chemistry, Faculty of Arts and Science, Bursa Uludağ University, Bursa, Turkey.

**E-Mail:** etumay@uludag.edu.tr

## INTRODUCTION

Phthalate acid esters (PAEs) are a group of chemicals that have been reported to have endocrine-disrupting effects in human and wildlife [1-4]. Because the phthalates are not chemically bound to the polymeric materials, they are easily leached from the product or during the manufacturing process to environment such as surface marine water, sediments, food, drugs and natural water [5]. Several PAEs were listed as priority pollutants by United States Environmental Agency, European Union and China National Environmental Monitoring Center due to their migration risks to the environment.

Diethyl phthalate (DEP) which is one of the important phthalate esters is used as a plasticizer for cellulose ester plastic films and sheets and molded and extruded articles. DEP has received growing attention in recent years, due to its toxicity, bioaccumulation rate and aqueous stability with a high hydrolysis half-life [6].

The removal of PAEs from aqueous systems to minimize their adverse effects is still an important and challenging task. Many different single or multiple technologies, such as adsorption [7,8], advanced oxidation [9-11] and biodegradation [12-13], have been proposed to treat PAEs contaminated water. Among these techniques, adsorption has been widely studied over recent years due to its high removal efficiency and cost-effectiveness. Thereby, a wide range of adsorbents was used for the water treatment like agricultural by-products, polymers, zeolites and activated carbons. Nowadays, the synthetic polymers have a great potential in the removal of PAEs, owing to their large surface areas, pore structures, mechanical rigidity and low-cost production. Until now, many polymeric resins, such as oxidized polystyrene resin (NDA-702), aminated polystyrene resin (NDA-101), macroporous polymer resin (XAD-4) and hyper-cross-linked polymer resins (NDA-99 and NDA-150), were used for removal of PAEs [14,15]. In our previous studies, cross-linked polymeric microbeads [16], magnetic polymeric microbeads [8], and polymeric nanobeads [17] were effectively used for removal of PAEs from the aqueous media.

The aim of this study is to investigate the efficiency of the poly(divinylbenzene-N-methacryloyl-L-tryptophan methyl ester) [poly(DVB-MATrp)] microbeads for removal of DEP from the aqueous phase. N-methacryloyl-L-tryptophan methyl ester (MATrp) and divinylbenzene (DVB) were used as a monomer and a cross-linker, respectively.

Suspension polymerization technique was preferred to obtain polymers in spherical form. To determine the efficiency of the poly(DVB-MATrp) microbeads to remove DEP from the aqueous phase, the effects of various experimental parameters such as operation pH, initial concentration, contact time and temperature on DEP adsorption were investigated. The nature of the adsorption process was evaluated via isothermal and kinetic models. In addition, bottled water and tap water samples spiked with DEP were used to show adsorption efficiency of the poly(DVB-MATrp) microbeads in real samples.

## MATERIALS and METHODS

### Chemicals

Diethyl phthalate (DEP) was purchased from Sigma-Aldrich. Divinylbenzene (DVB) was obtained from Merck (Darmstadt, Germany). Methacryloyl chloride, L-tryptophan methyl ester and 2,2'-azobisisobutyronitrile (AIBN) were purchased from Sigma Chemical Co. (St. Louis, USA). All other chemicals were of reagent grade. All water used in the binding experiments was purified using a Elga Flex3 ultrapure water instrument (Veolia Water Solutions & Technologies, France).

### Synthesis and Characterization of Poly(DVB-MATrp) Microbeads

N-methacryloyl-L-tryptophan methyl ester (MATrp) was used as a monomer and synthesized as previously described [18]. Poly(DVB-MATrp) microbeads were synthesized by suspension polymerization. The suspension polymerization recipe for the preparation of the poly(DVB-MATrp) microbeads was provided in Table 1. The characterization studies of the microbeads were conducted by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), elemental analysis and swelling test. FTIR spectrum of the poly(DVB-MATrp) microbeads was recorded in the range of 400-4000  $\text{cm}^{-1}$  (Perkin Elmer, Spectrum 100, USA). A scanning electron microscope (Jeol, JEM 1200EX, Tokyo, Japan) was used to investigate the surface morphology of the microbeads. Elemental analysis was performed to determine the elemental composition of the poly(DVB-MATrp) microbeads (Leco, CHNS-932, USA). The swelling ratio of the microbeads was determined as follows. Firstly, dry microbeads were weighed and put into a 50 mL of distilled water. The vial including the poly(DVB-MATrp) microbeads was incubated in the water bath with a fixed temperature ( $25 \pm 0.5^\circ\text{C}$ ) for 8 h. The microbeads taken from the water were dried

**Table 1.** Polymerization recipe for preparation of the poly(DVB-MATrp) microbeads.

Dispersion phase	Organic phase	Polymerization conditions
Distilled water (50 mL)	DVB (3.77 mL)	Reactor volume (100 mL)
Poly (vinyl alcohol) (200 mg)	MATrp (0.88 mL)	Stirring rate (400 rpm)
	Toluen (3.5 mL)	Temperature (80°C)

with filter paper and weighed. The dry weight and wet weight of the poly(DVB-MATrp) microbeads were used to calculate the swelling ratio.

### Batch Adsorption Procedure

The DEP solution at a concentration of 500 mg/L was prepared by dissolving the required amounts of DEP in pure water and kept in a refrigerator at 4°C. Then, the stock solution was appropriately diluted to get test solutions at desired concentrations. These solutions were analyzed by a double-beam UV–visible spectrophotometer (UV-1700 Shimadzu,  $\lambda_{\max} = 239$  nm). All adsorption studies were conducted in discontinuous mode by using the same experimental protocol. In an Erlenmeyer, appropriate amounts of the poly(DVB-MATrp) microbeads were added to 50 mL of DEP solutions via temperature-controlled incubator system (Heidolph Instruments, GmbH & Co. KG, Schwabach, Germany). The mixture was stirred at constant speed (300 rpm) for 8h. Subsequently, the aliquots were filtered through a 0.45  $\mu\text{m}$  polytetrafluoroethylene membrane and analyzed by UV– visible spectrophotometer. The adsorption capacity  $q_e$  (mg/g) was calculated from the relation:

$$q_e = \frac{(C_0 - C_t)V}{m_{ads}} \quad (1)$$

where  $C_0$  and  $C_t$  (mg/L) are the initial and the residual concentration at time  $t$  (min), respectively.  $m_{ads}$  (g) is the amount of adsorbent and  $V$  (L) is the volume of the DEP solution.

To optimize the experimental conditions, the operating parameters were studied as follows: (1) the influence of pH on DEP adsorption onto the poly(DVB-MATrp) microbeads was studied by varying the initial pH of solutions in the range of 2.0 to 10.0. The initial DEP concentration was 20 mg/L. The pH of the medium was adjusted by using 0.1 M HCl and 0.1 M NaOH solutions; (2) to investigate the effect of initial DEP concentration on adsorption capacity, the concentration of DEP was varied from 1.0 mg/L to 300 mg/L at pH 3.0; (3) the adsorption

kinetics was determined by analyzing the uptake of the DEP from aqueous solution at different time intervals for 180 min at a initial DEP concentration of 20 mg/L (pH 3.0). The effects of initial DEP concentration and contact time were investigated at three different temperatures (25°C, 35°C and 45°C).

The Langmuir and Freundlich isotherm models were used to investigate isotherm data. The linearized form of Langmuir equation can be given in Eq. (2): [19]

$$\frac{C_e}{q_e} = \frac{1}{Q_L K_L} + \frac{C_e}{Q_L} \quad (2)$$

where  $q_e$  is the adsorption capacity at equilibrium (mg/g),  $C_e$  is the equilibrium concentration of DEP (mg/L) and  $K_L$  is the Langmuir equilibrium constant related to the affinity of binding sites (L/mg). Also, the essential characteristic of the Langmuir isotherm can be expressed by a dimensionless separation factor,  $R_L$ :

$$R_L = \frac{1}{1 + K_L C_e} \quad (3)$$

The linearized form of Freundlich isotherm can be expressed as: [20]

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

where  $C_e$  is the equilibrium concentration of DEP (mg/L),  $K_f$  (mg/g)(L/mg) $^{1/n}$  and  $n$  are isotherm constants that indicate capacity and intensity of the adsorption, respectively.

The kinetics of adsorption process was investigated by using pseudo-first-order and pseudo-second-order models. The linear forms of the applied pseudo-first-order model [21] and pseudo-second-order model [22] can be expressed as the following equations, respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where  $q_e$  and  $q_t$  (mg/g) are the amounts of DEP adsorbed at equilibrium and at time  $t$  (min), respectively.  $k_1$  (1/min) and  $k_2$  ((g/mg)/min) are rate constants for pseudo-first-order and pseudo-second-order kinetic models, respectively.

### Desorption Studies

Reusability of the poly(DVB-MATrp) microbeads for DEP adsorption was investigated via successive adsorption/desorption cycles. A methanol–acetic acid (9:1 v/v) solution was used as a desorption agent. The DEP adsorption/desorption cycle was repeated five times using the same microbeads. The initial DEP concentration was 20 mg/L (pH 3.0, 50 mL). After the adsorption step, the poly(DVB-MATrp) microbeads were incubated with the desorption solution (50 mL) for 3 h. The microbeads were centrifuged at 5000 rpm (10 min) and the supernatant was used to determine the desorbed amount of DEP. Then, the microbeads were washed with excess amount of water and used for DEP adsorption again.

### Removal of DEP from Real Water Sample

The bottled and tap water samples were used to evaluate the effectiveness of poly(DVB-MATrp) microbeads

in real water sample. The water samples spiked with DEP (20 mg/L) were incubated with poly(DVB-MATrp) microbeads. Different amounts of poly(DVB-MATrp) microbeads (0.02–0.06 g) were separately added to the solutions. For each sample, three replicate experiments were performed. The removal efficiency  $R$  (%) was calculated according to Eq (7)

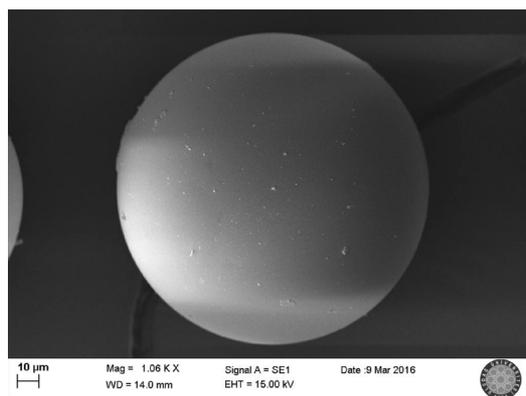
$$R\% = \frac{(C_0 - C_t)}{C_0} 100 \quad (7)$$

where  $C_0$  and  $C_t$  (mg/L) are the initial concentration and the residual concentration at time  $t$  (min), respectively.

## RESULTS and DISCUSSION

### Properties of Poly(DVB-MATrp) Microbeads

The suspension polymerization procedure enabled to obtain poly(DVB-MATrp) microbeads in spherical form. The SEM image provided in Figure 1 clearly demonstrated the success of applied polymerization procedure. The size of the poly(DVB-MATrp) microbeads ranged 150–200  $\mu\text{m}$  in diameter. The characteristics of the poly(DVB-MATrp) microbeads were summarized in Table 2. FTIR analysis of the poly(DVB-MATrp) microbeads demonstrated that the microbeads were



**Figure 1.** SEM photograph of the poly(DVB-MATrp) microbead.

**Table 2.** The characteristics of the poly(DVB-MATrp) microbeads.

Swelling ratio	17%
Elemental composition	81.5% C, 7.69% H, 0.61% N.
Size	150–200 $\mu\text{m}$ in diameter
FTIR analysis	C=C stretching at 1444 $\text{cm}^{-1}$ , 1486 $\text{cm}^{-1}$ , 1511 $\text{cm}^{-1}$ , 1605 $\text{cm}^{-1}$ and 1699 $\text{cm}^{-1}$ Benzene ring deformations at 700–750 $\text{cm}^{-1}$ C-H (aliphatic) stretching at 2870–3000 $\text{cm}^{-1}$ C-H (aromatic) stretching at 3057 $\text{cm}^{-1}$ N-H stretching vibration at 3400 $\text{cm}^{-1}$

successfully synthesized. Swelling ratio of the poly(DVB-MATrp) microbeads was determined as 17% probably resulting from low porosity and also non-polar chemistry of the cross-linker (DVB) and monomer (MATrp) used in the preparation of the microbeads. Although the low swelling ratio appears to be a disadvantage to obtain a high adsorption capacity, it will accelerate the adsorption/desorption process as the process occurs near the surface of the microbeads. In addition, the affinity of DEP molecule to the poly(DVB-MATrp) microbeads can be high due to the non-polar moieties in the DEP molecule.

### Parameters Affecting the DEP Adsorption

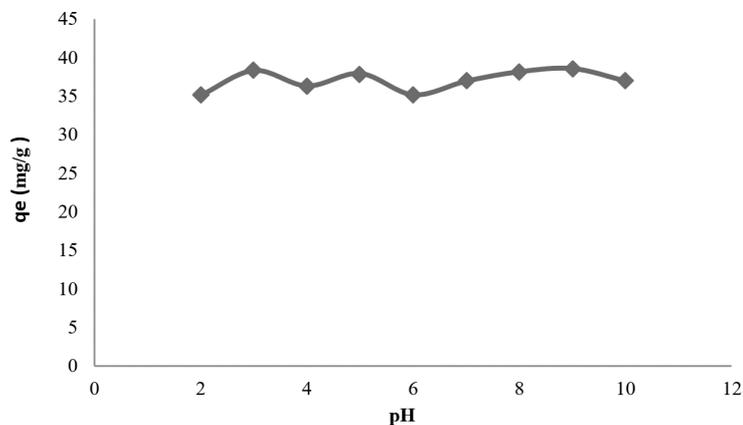
#### pH Effect

The pH of adsorption medium is an important parameter affecting the adsorption capacity. Thus, DEP solutions (20 mg/L) prepared in the pH range of 2.0 to 10.0 were incubated with poly(DVB-MATrp) microbeads.

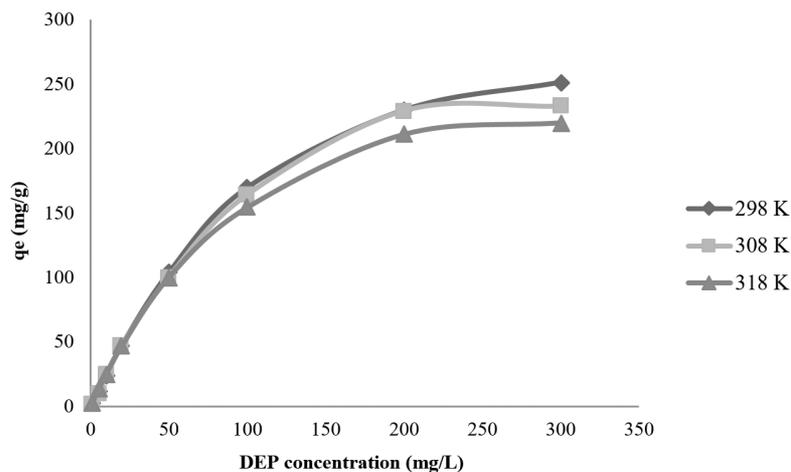
The adsorbed amounts of DEP at different pHs were provided in Figure 2. The results clearly showed that the pH of the medium did not significantly affect the adsorption capacity of the microbeads. Actually, the solution pH is particularly significant when the adsorbent and/or adsorbate molecule contain ionizable groups. However, neither the DEP molecule in the solution nor the MATrp molecule in the structure of poly (DVB-MATrp) microbeads has a net charge in the studied pH range. The result provides a strong evidence that DEP molecules were adsorbed onto the poly (DVB-MATrp) microbeads via hydrophobic and Van der Waals interactions.

#### Initial DEP Concentration Effect

Batch adsorption experiments were performed in the DEP concentration range of 1-300 mg/L at pH 3.0. The adsorbed amounts of DEP at three different temperatures (298 K, 308 K and 318 K) were provided in Figure 3. The DEP adsorption capacity of the



**Figure 2.** Effect of pH on DEP adsorption onto the poly(DVB-MATrp) microbeads (initial DEP concentration: 20 mg/L, solution volume: 50 mL and incubation temperature: 25°C).



**Figure 3.** Effect of initial DEP concentration on adsorption of DEP onto the poly(DVB-MATrp) microbeads (pH: 3.0, solution volume: 50 mL and incubation temperature: 25°C, 35°C and 45°C).

poly(DVB-MATrp) microbeads increased from 2.8 mg/g to 251.3 mg/g for 298 K in the studied concentration range. The DEP adsorption capacity of the poly(DVB-MATrp) microbeads was compared with that of other adsorbents in Table 3. It seems that poly(DVB-MATrp) microbeads offers a comparable adsorption capacity for DEP. The temperature effect was also monitored to reveal the nature of adsorption. The thermal variation, examined at three temperatures: 298 K, 308 K and 318 K, has a moderate effect onto the adsorption capacity which decreases slightly from 251.3 mg/g to 220.2 mg/g with increasing temperature (Figure 3). Thus, lower temperatures promote the DEP removal suggesting that the adsorption process is exothermic in nature.

The Langmuir and Freundlich isotherm models in their linear forms were used to analyze the adsorption equilibrium of DEP. The parameters obtained from isotherm models were summarized in Table 4. Langmuir isotherm fitted the experimental data with high correlation coefficients ( $0.9927 < R^2 < 0.9957$ ) for three

different temperatures (298 K, 308 K and 318 K). In addition, the calculated DEP adsorption capacities were close to the experimental adsorption capacities. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of active sites on the poly (DVB–MATrp) microbeads' surface since the Langmuir equation assumes that the surface is homogeneous [19].

Furthermore, the essential characteristic of the Langmuir isotherm can be expressed by a dimension-less separation factor called equilibrium parameter ( $R_L$ ). The calculated  $R_L$  values were all less than unity demonstrating the favorable adsorption in the experimental conditions. On the contrary, the Freundlich isotherm model is based on the assumption that the adsorption occurs in multilayers with heterogeneous adsorbent surfaces [20]. Based on the correlation coefficients ( $0.7190 < R^2 < 0.86467$ ) obtained for three different temperature, the adsorption data were not well fitted by Freundlich isotherm (Table 4). As a result, the best fitting of the equilibrium data was obtained

**Table 3.** Comparison of adsorption capacities with other adsorbents.

Adsorbent	$q_{max}$ (mg/g)	Adsorption time (min)	pH-Temperature(°C)	References
Magnetic poly(ethylene glycol dimethacrylate–vinyl pyridine), (mag-poly(EGDMA–VP)) beads	98.9	45	3.0/25	[8]
NDA-99 (resin)	314	1440	7.0/25	[14]
Poly(ethylene glycol dimethacrylate-N-methacryloyl-L-tryptophan methyl ester) [poly(EGDMA-MATrp)]	590.7	180	3.0/25	[16]
Mineral rich waste coal modified with chitosan	42.7	300	5.8/25	[23]
Activated carbon from Albizzia julibrissin pods	438	60	3.8/25	[24]
Zeolith ZIF-8	44.7	-	3.5/25	[25]
Commercial activated carbon	184.2	1440	3.5/25	[25]
ACS-2 resin	515.7	1440	4.0-11.5/25	[26]
Poly(DVB-MATrp)	251.3	30	3.0/25	In this study

**Table 4.** Isotherm results at different temperatures.

Temperature	298 K	308 K	318 K
Langmuir model			
$q_{max}$ (mg/g)	253	243	228
$q_e$ (mg/g)	251.3	232.6	220.2
$K_L$ (L/mg)	0.1727	0.1133	0.1061
$R^2$	0.9957	0.9934	0.9927
$R_L$	0.0189	0.0286	0.0305
Freundlich model			
1/ n	0.4617	0.4154	0.3580
$K_F$ (mg/g)(L/mg) <sup>1/n</sup>	30.9	30.5	22.6
$R^2$	0.8647	0.7611	0.7190

with the Langmuir model suggesting that the adsorption process occurs favorably on a monolayer.

### Contact Time Effect

The effect of contact time on DEP adsorption onto the poly (DVB-MATrp) microbeads was provided in Figure 4. The adsorption rates were fast at all studied temperatures. The adsorption reached equilibrium at around 30 min. The adsorption process can be divided into rapid and slow steps. In the first step, DEP molecules were adsorbed rapidly onto the exterior surface of poly (DVB-MATrp) microbeads owing to the abundance of free binding sites. Hence, the adsorbent surface was nearly saturated with DEP molecules which affect the rate of second step that the DEP molecules diffused from the external surface to the inner sites of the adsorbent [6].

Additionally, the adsorbed amount of DEP decreased with increasing temperature (Figure 4). The result demonstrated that the adsorption was exothermic in nature. To determine the adsorption dynamics, two kinetic models, namely the pseudo-first order [21] and pseudo second order [22], were used to evaluate the adsorption process. The values of the parameters and correlation coefficients obtained from these kinetic models were all

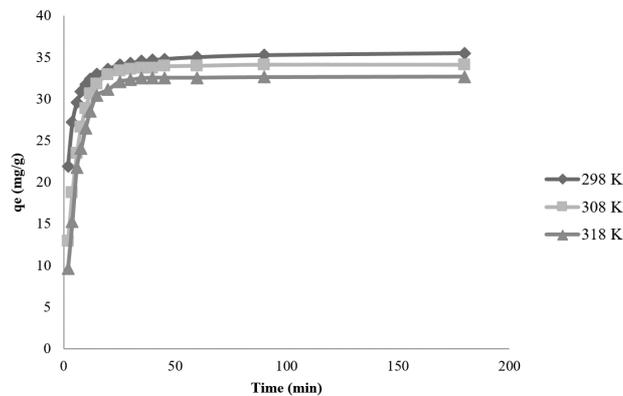
listed in Table 5. The higher correlation coefficients ( $0.9991 < R^2 < 0.9999$ ) of pseudo-second-order kinetic model for all temperatures and the closest  $q_e$  (experimental) to  $q_e$  (calculated) indicated the second-order nature of the present adsorption process.

### Reusability of the Poly(DVB-MATrp) Microbeads

The DEP adsorption capacities of the poly(DVB-MATrp) microbeads for five successive adsorption/desorption cycles were determined as 38.3, 37.8, 37.6, 36.7 and 36.9 mg DEP/g polymer, respectively. The results showed that the adsorbed amount of DEP onto the poly(DVB-MATrp) microbeads did not significantly change after five successive adsorption/desorption cycles. Thus, it can be concluded that the poly(DVB-MATrp) microbeads can be repeatedly used for DEP adsorption.

### Real Sample Analysis

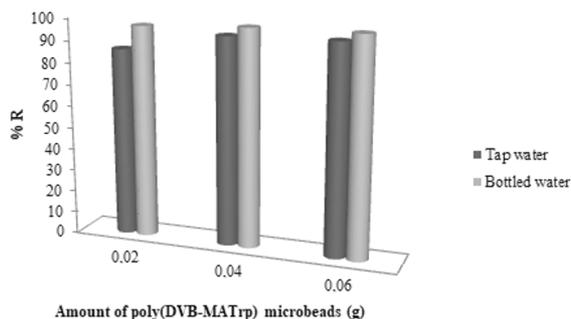
The real water samples were also used to determine matrix effect since the components of water samples from different sources differ from pure water. These components can affect the adsorption capacity of the adsorbent. Two water samples (bottled water and tap water) spiked with DEP solution (20 mg/L) were used to investigate the efficiency of the poly(DVB-MATrp) microbeads in the real samples. The removal efficiencies (R%) were depicted in Figure 5. The DEP



**Figure 4.** Effect of contact time on DEP adsorption onto the poly(DVB-MATrp) microbeads (initial DEP concentration: 20 mg/L, solution volume: 50 mL, pH: 3.0 and incubation temperature: 25°C, 35°C and 45°C).

**Table 5.** Kinetic parameters for the adsorption of DEP onto the microbeads.

Parameters		Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Temperature	Experimental	$k_1 \times 10^2$ (1/min)	$q_{eq}$ (mg/g)	$R^2$	$k_2 \times 10^2$ ((g/mg)/min)	$q_{eq}$ (mg/g)	$R^2$
277	35.53	5.33	7.42	0.9008	2.22	35.78	0.9999
298	34.09	9.33	13.24	0.9211	1.63	34.64	0.9996
318	32.70	10.50	15.68	0.9032	1.33	33.39	0.9991



**Figure 5.** Removal efficiencies of DEP with different amount of poly(DVB-MATrp) microbeads.

removal efficiencies in tap and bottled water samples fell in the range of 86.08% to 98.90%. The higher the amount of adsorbent, the higher the adsorbed amount of DEP onto the poly(DVB-MATrp) microbeads. The repeatabilities expressed as the relative standard deviations (RSDs) varied from 0.09% to 5.85%. The results showed that the poly(DVB-MATrp) microbeads can be effectively used for DEP adsorption from real water samples.

## CONCLUSION

In this study, the effectiveness of hydrophobic poly(DVB-MATrp) microbeads for DEP removal from aqueous phase was investigated. The poly(DVB-MATrp) microbeads had a high adsorption capacity for DEP with a maximum adsorption amount of 251.3 mg DEP/g polymer at 25°C. The adsorption process was exothermic. The adsorption data were fitted with the Langmuir isotherm model and pseudo-second-order kinetic model. The adsorbed DEP molecules can be rapidly desorbed probably due to the low porosity of the microbeads. As a result, the poly(DVB-MATrp) microbeads can be used for successive adsorption of DEP from aqueous solution. The matrix of real water samples did not affect the DEP adsorption capacity of the poly(DVB-MATrp) microbeads. The results obtained in the study demonstrated the usability of poly(DVB-MATrp) microbeads for DEP removal from water.

### Acknowledgments

This work was supported by the Scientific and Technological Research Council of Turkey and was assigned project number 118 Z 021.

## References

1. A. Charles Staples, R. Dennis Peterson, F. Thomas Parkerton, J. William Adams, The environmental fate of phthalate esters: a literature review, *Chemosphere*, 35 (1997) 667-749.
2. J. Manori Silva, E. Samandar, A. John Reidy, R. Hauser, L. Larry Needham, M. Antonia Calafat, Metabolite profiles of di-n-butylphthalate in humans and rats, *Environ. Sci. Technol.*, 41 (2007) 7576-7580.
3. K. Kelly Ferguson, R. Loch-Caruso, D. John Meeker, Urinary phthalate metabolites in relation to biomarkers of inflammation and oxidative stress: NHANES 1999-2006, *Environ. Res.*, 111 (2011) 718-726.
4. K. Selma Kranich, H. Frederiksen, A. Maria Andersson, N. Jørgensen, Estimated daily intake and hazard quotients and indices of phthalate diesters for Young danish men, *Environ. Sci. Technol.*, 48 (2013) 706-712.
5. L. Emma Bradley, A. Richard Burden, I. Leon, N. David Mortimer, R. Dennis Speck, L. Castle, Determination of phthalate diesters in foods, *Food Addit. Contam. A*, 30 (2013) 722-734.
6. Y. Bouhamidi, F. Kaouah, L. Nouri, S. Boumaza, M. Trari, Adsorption of diethyl and dibutylphthalates onto activated carbon produced from Albiziajulibrissin pods: kinetics and isotherms, *Int. J. Environ. Sci. Technol.*, 14 (2017) 271-284.
7. S. Venkata Mohan, S. Shailaja, M. Rama Krishna, P.N. Sarma, Adsorptive removal of phthalate ester (Di-ethylphthalate) from aqueous phase by activated carbon: a kinetic study, *J. Hazard. Mater.*, 146 (2007) 278-282.
8. E. Tümay Özer, B. Osman, A. Kara, N. Beşirli, Ş. Gücer, H. Sözeri, Removal of diethylphthalate from aqueous phase using magnetic poly (EGDMA-VP) beads, *J. Hazard. Mater.*, 229 (2012) 20-28.
9. N. Chen, G. Fang, D. Zhou, J. Gao, Effects of clay minerals on diethylphthalate degradation in Fenton reactions, *Chemosphere*, 165 (2016) 52-58.
10. K. Muzamil Gani, A. Ahmad Kazmi, Phthalate contamination in aquatic environment: A critical review of the process factors that influence their removal in conventional and advanced wastewater treatment, *Critical Reviews In Environmental Science and Technol.*, 46 (2016) 1402-1439.

11. I. Gultekin, N.H.Ince, Synthetic endocrine disruptors in the environment and water remediation by advanced oxidation processes, *J. Environ. Manag.*, 85 (2007) 816-832.
12. Z. Dan Wen, D. Wen Gao, W. MinWu, Biodegradation and kinetic analysis of phthalates by an *Arthrobacter* strain isolated from constructed wet land soil, *Appl. Microbiol. Biotechnol.*, 98 (2014) 4683-4690.
13. N. Singh, V. Dalal, J. Krishna Mahto, P. Kumar, Biodegradation of phthalic acid esters (PAEs) and in silico structural characterization of mono-2-ethylhexyl phthalate (MEHP) hydrolase on the basis of close structural homolog, *J. Hazard. Mater.*, 338 (2017) 11-22.
14. Z. Xu, W. Zhang, B. Pan, C. Hong, L. Lv, Q. Zhang, B. Pan, Q. Zhang, Application of the Polanyi potential theory to phthalates adsorption from aqueous solution with hyper-cross-linked polymer resins, *J. Colloid Interface Sci.*, 319 (2008) 392-397.
15. Z. Xu, W. Zhang, B. Pan, L. Lv, Z. Jiang, Treatment of aqueous diethylphthalate by adsorption using a functional polymer resin, *Environ. Technol.*, 32 (2011) 145-153.
16. E.Tümay Özer, B. Osman, A. Kara, E. Demirbel, N. Beşirli, Ş. Güçer, Diethylphthalate removal from aqueous phase using poly(EGDMA-MATrp) beads: kinetic, isothermal and thermodynamic studies, *Environ. Technol.*, 36 (2015) 1698-1706.
17. E. Tümay Özer, A. Göçenoğlu Sarıkaya, B. Osman, Adsorption and removal of diethylphthalate from aqueous media with poly(hydroxyethylmethacrylate) nanobeads, *Desalin. Water Treat.*, 57 (2016) 28864-28874.
18. B. Osman, L. Uzun, N. Beşirli and A. Denizli, Microcontact imprinted surface Plasmon resonance sensor for myoglobin detection, *Mater. Sci. Eng. C*, 33 (2013) 3609-3614.
19. I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I. Solids, *J. Am. Chem. Soc.*, 38 (1916) 2221-2295.
20. H.M.F. Freundlich, Over the adsorption in solution, *J. Phys. Chem.*, 57 (1906) 385-471.
21. S. Lagergren, Zur theorie der sogenannten Adsorption gelöster stoffe, *Kungliga Svenska Vetenskapsakademiens Handlingar* 25 (1898) 1-39.
22. Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, *Process Biochem.*, 34 (1999) 451-465.
23. M. A. Shaida, R.K. Dutta, A.K. Sen, Removal of diethyl phthalate via adsorption on mineral rich waste coal modified with chitosan, *Journal of Molecul. Liquids*, 261 (2018) 271-282.
24. Y. Bouhamidi, F. Kaouah, L. Nouri, S. Boumaza, M. Trari & Z. Bendjam, Kinetic, thermodynamic, and isosteric heat of dibutyl and diethyl phthalate removal onto activated carbon from *Albizia julibrissin* pods, *Particul. Sci. Technol.*, 36 (2018) 235-243.
25. N.A. Khan, B.K. Jung, Z. Hasan, S.H. Jhung, Adsorption and removal of phthalic acid and diethyl phthalate from water with zeolitic imidazolate and metal-organic frameworks, *J. Hazard. Mater.* 282 (2015)194-200.
26. Q. Shi, A. Li, Q. Zhou, C. Shuang, Y. Li, Removal of diethyl phthalate from aqueous solution using magnetic iron-carbon composite prepared from waste anion exchange resin, *J. Taiwan Inst. Chem. Eng.*, 45 (2014) 2488-2493.